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# Acid-base triggered switching of circularly polarized luminescence and electronic circular dichroism in organic and organometallic helices

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**Abstract:** Electronic circular dichroism and circularly polarized luminescence acid-base switching activity is demonstrated in helicene-bipyridine proligand (**1a**) and in its "rollover" cycloplatinated derivative (**2a**). While proligand **1a** displays a strong bathochromic shift (>160 nm) of the non polarized and circularly luminescence upon protonation, complex **2a** displays slightly stronger emission. This striking different behavior between singlet emission in the organic helicene and triplet emission in the organometallic one is rationalized using theory. The very large bathochromic shift of the emission observed upon protonation of azahelicene-bipyridine **1a** was rationalized by the decrease of aromaticity (promoting a charge transfer-type transition rather than a  $\pi-\pi^*$  one) along with an increase of the HOMO-LUMO character of the transition and stabilization of the LUMO level upon protonation.

## Introduction

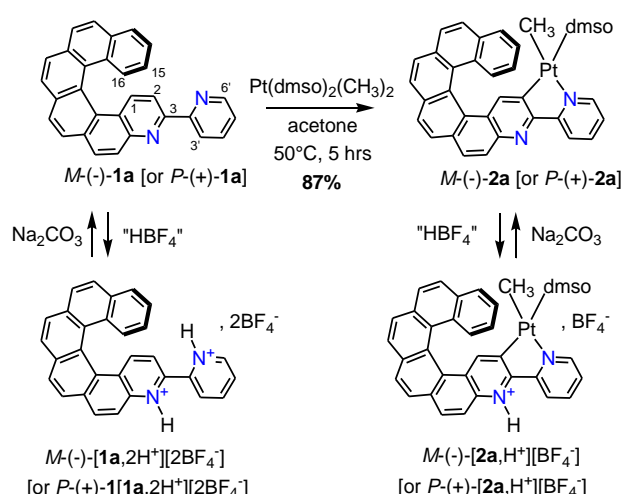
The development of chiral molecules displaying large chiroptical properties may lead to novel multifunctional molecular materials.<sup>[1]</sup> In this area, helices show great potential. Due to their  $\pi$ -conjugated helical backbone, they combine high optical activity with other properties such as intense emission.<sup>[2,3]</sup> Recently, organometallic helices in which a transition metal (Pt, Ir, Os) is included within the helical  $\pi$ -framework have emerged as promising candidates for opto-electronic applications and as good chiral emitters.<sup>[3e,4]</sup> Devices displaying circularly polarized luminescence (CPL) are of great interest since CPL activity may be a powerful method to address encoded information (cryptography) or for 3D displays.<sup>[5a]</sup> More generally, systems that possess switchable CPL functionality

may lead to new possibilities for molecular information processing and storage.<sup>[5b]</sup>

In this paper, we describe the regioselective rollover cycloplatination of a helicene-2,2'-bipyridine proligand,<sup>[6]</sup> namely 3-(2-pyridyl)-4-aza[6]helicene (**1a**), Scheme 1. The new organic and organometallic helicene derivatives act as unprecedented multifunctional pH-switchable chemical systems due to the reversible tuning of their optical and chiroptical properties: optical rotation (OR), electronic circular dichroism (ECD), non-polarized luminescence and CPL. The different behaviors of these ECD and CPL switches are interpreted based on results from first-principles calculations.

## Results and Discussion

The synthesis of racemic 3-(2-pyridyl)-4-aza[6]helicene **1a** was performed in two steps from 2,2'-bipyridine-6-carboxaldehyde, by a Wittig reaction with 2-methylbenzophenanthrene phosphonium bromide<sup>[7]</sup> followed by a photocyclization reaction (83% overall yield),<sup>[2]</sup> and enantiopure *M*- and *P*-**1a** (*ee*'s >99%) were subsequently obtained by HPLC over a Chiralpak IC stationary phase (see Supporting Information, SI).



**Scheme 1.** Synthesis of enantiopure rollover cycloplatinated  $\text{Pt}(\text{CH}_3)(\text{dmsO})(\text{bipy}-\text{H})$  complexes *M*(-)- and *P*(+)-**2a** from enantiopure helicene-bipy proligands *M*(-)- and *P*(+)-**1a**. Reversible protonation/deprotonation in acetone.

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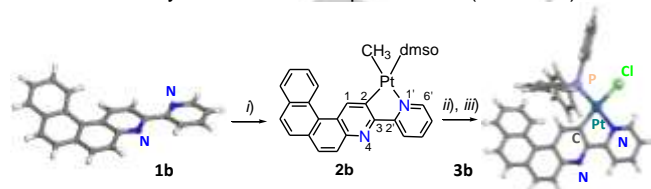
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3-(2-Pyridyl)-4-aza[6]helicene (**1a**) has been fully characterized and displays classical spectroscopic features of helicenes (see Experimental Part). The X-ray crystallographic structure of a smaller model molecule, *i.e.* 3-(2-pyridyl)-4-aza[4]helicene **1b** displayed in Scheme 2 shows *i)* the helical aza[4]helicene part (helicity 25.13°), *ii)* the grafted 2-pyridyl group which is coplanar with the helicene part (dihedral angles of -1.17 and 5.35 between the two pyridyl rings) and *iii)* the two nitrogen atoms in mutually *trans* positions.

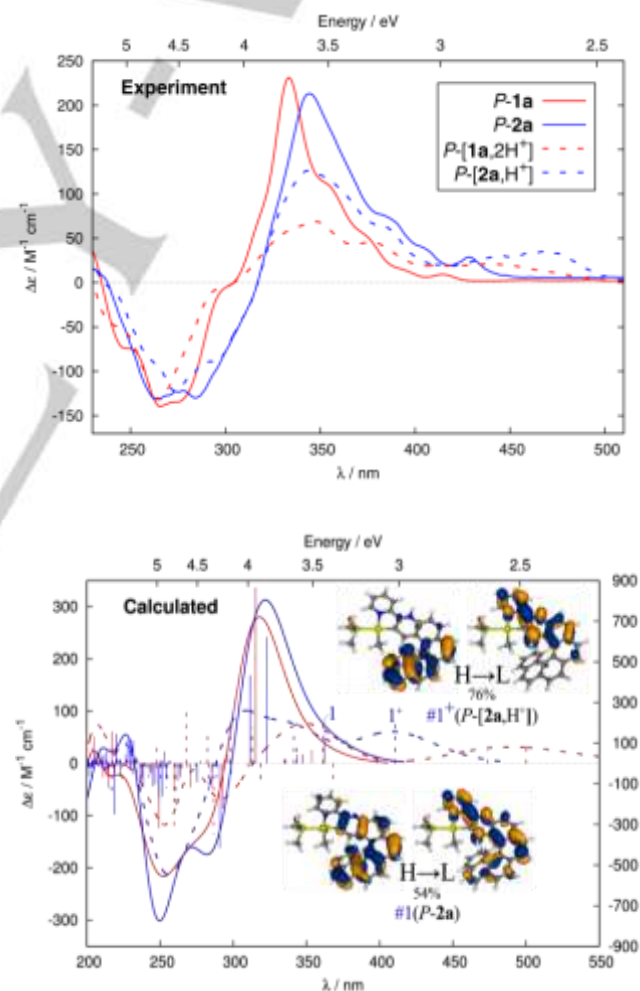
Examples of molecular materials based on chiral bipy ligands and their complexes are still rare.<sup>[8]</sup> Apart from their common 1,4-*N,N* chelating behavior, 2,2'-bipyridines can act as 1,4-*C,N* chelates through the direct metal-mediated C-H bond activation at the 3-position of the 2-pyridyl ring and undergo the so-called "rollover" cyclometalation.<sup>[9,10]</sup> The *N'*-C<sup>2</sup> rollover cycloplatination of *M*- and *P*-**1a** to enantiopure complexes *M*- and *P*-**2a** (Scheme 1) was performed by reacting respectively *M*- and *P*-**1a** with electron-rich [Pt(dmsO)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>] precursor at 50°C in acetone for 5 hours (87% yield). The formation, regioselectivity, and stereochemistry of the neutral square-planar Pt(II) complex **2a** was established by multinuclear NMR spectroscopy. For example, the <sup>1</sup>H NMR spectrum at 400 MHz revealed the disappearance of the H<sup>2</sup> signal, the strong deshielding (1 ppm) of proton H<sup>6</sup> (9.5 ppm) with satellites due to a <sup>3</sup>*J*(<sup>195</sup>Pt, <sup>1</sup>H) coupling constant of 20 Hz, and the H<sup>1</sup> proton appearing at 8.1 ppm with a <sup>3</sup>*J*(<sup>195</sup>Pt, <sup>1</sup>H) of 63 Hz, all confirming the C<sup>2</sup>-Pt and N<sup>1</sup>-Pt bond formation. These results show that the CH activation process proceeded regioselectively at the C<sup>2</sup> position only.<sup>[10]</sup> Due to *trans* effects, the cycloplatination is also stereoselective, with the dmsO S-ligand placed *trans* to the C<sup>2</sup> carbon. Note that the Pt-CH<sub>3</sub> signal appears at -0.34 ppm (<sup>2</sup>*J*(<sup>195</sup>Pt, <sup>1</sup>H) = 83 Hz) while the two dmsO methyl groups are diastereotopic with the <sup>3</sup>*J*(<sup>195</sup>Pt, <sup>1</sup>H) coupling constant (18 Hz).<sup>[10]</sup> Using the same conditions as for **2a**, the regio- and stereoselective *N'*-C<sup>2</sup> rollover cycloplatination of model proligand **1b** gave complex **2b** with 89% yield (Scheme 2). This compound displayed the same spectroscopic features as **2a**. Furthermore, reaction of complex **2b** with HCl (0.1N) followed by reaction with triphenylphosphine, yielded complex **3b** in which the PPh<sub>3</sub> ligand is *trans* to the N<sup>1</sup> nitrogen and a chlorine is placed *trans* to the C<sup>2</sup> carbon.<sup>[10d]</sup> The X-ray crystallographic structure of **3b** finally ascertained the presence of the platinacycle (Scheme 2).<sup>[11]</sup> Noteworthy, very low dihedral angles (2-3°) between the two pyridyl rings ensure that the π-conjugation extends across the whole molecule. The N atom of the helical moiety remains free for protonation (*vide infra*).<sup>[10e]</sup>



**Scheme 2.** Reactivity of rollover cycloplatinated Pt(CH<sub>3</sub>)(dmsO)(bipy-H) complex **2b**. *i)* Pt(dmsO)<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>, acetone, 50°C, 5 hrs, 89%. *ii)* HCl (0.1N), acetone, dmsO, 8 hrs, 70%; *iii)* PPh<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 2 hrs, 98%. X-ray crystallographic structures of proligand **1b** and of cycloplatinated complex **3b**.

Azahelicenes are known to exhibit high proton affinities<sup>[12]</sup> and some of them behave as proton sponges,<sup>[12b]</sup> while,

according to Zucca *et al.*, in the protonated rollover cycloplatinated complex the ligand may be considered as an "abnormal remote heterocyclic chelated carbene or simply as mesoionic cyclometalated ligand".<sup>[10e]</sup> Therefore, in our quest for original new organometallic helicene-based chiroptical switches,<sup>[13a,14]</sup> we investigated the acid-base reactivity and the use of organic helicene **1a** and cycloplatinated helicene **2a** as potential multifunctional pH-triggered UV-vis, OR, ECD and/or CPL switches. The acid [H<sub>2</sub>O.HBF<sub>4</sub>]<sub>2</sub>[18C6] ("HBF<sub>4</sub>")<sup>[10d,15]</sup> in acetone or CH<sub>2</sub>Cl<sub>2</sub> was used to protonate either proligand **1a** or rollover complex **2a** into respectively *M*-(-) and *P*-(+) enantiopure forms of [1a,2H<sup>+</sup>][2BF<sub>4</sub><sup>-</sup>] and [2a,H<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] while treatment with Na<sub>2</sub>CO<sub>3</sub> or NEt<sub>3</sub> enabled the recovery of the neutral forms (Scheme 1). The unusual electronic properties of these systems were rationalized with the help of density functional theory (DFT) and time-dependent DFT, using the B3LYP functional (50% exact exchange) and a split-valence basis with polarization functions for non-hydrogen atoms (SV(P)) for most calculations. Computational details, detailed analyses, and additional results not discussed herein, are provided in the Supplementary Information (SI).



**Figure 1.** Measured (up, CH<sub>2</sub>Cl<sub>2</sub>, ~10<sup>-5</sup> M) and calculated (bottom) B3LYP CD spectra of proligand *P*-**1a** (plain red), *P*-[1a,2H<sup>+</sup>][2BF<sub>4</sub><sup>-</sup>] (dotted red), and of complexes *P*-**2a** (plain blue) *P*-[2a,H<sup>+</sup>][BF<sub>4</sub><sup>-</sup>] (dotted blue). Frontier MOs (0.03 au) of *P*-**2a** and *P*-[2a,H<sup>+</sup>]. For assignments of the spectra see the SI.

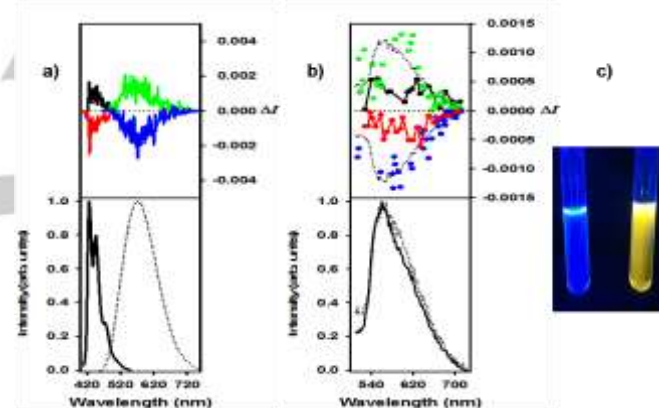
The UV-vis absorption spectrum of **1a** (SI) is typical of an extended  $\pi$ -conjugated system, with a strong band ( $\epsilon > 50 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ ) at 266 nm, and several structured broad bands around 330, 350 and 393 nm. Proligand **P-1a** displays a strong, structured, negative CD band at c.a. 264 nm ( $\Delta\epsilon = -183 \text{ M}^{-1} \text{ cm}^{-1}$ ) and strong positive bands at 333, 352 and 375 nm ( $\Delta\epsilon = +235, +107, +42 \text{ M}^{-1} \text{ cm}^{-1}$ ), Figure 1. These values are stronger than for unsubstituted 4-aza[6]helicene,<sup>[13]</sup> owing to the extended  $\pi$ -conjugation and partial charge transfer (CT) character of the lowest-energy  $\pi$ - $\pi^*$  excitations (dominantly from the highest occupied molecular orbital (HOMO, H, Figure 3) to the lowest unoccupied MO (LUMO, L). A high molar rotation is observed for **1a** (**P-1a**:  $[\phi]_D = +12000^\circ \text{ cm}^2 \text{ dmol}^{-1}$  ( $\pm 5\%$ ), in  $\text{CH}_2\text{Cl}_2$ ,  $6.5 \times 10^{-5} \text{ M}$ , calc. B3LYP +14176).

Proligand **1a** exhibits emission behavior typical of  $\pi$ -conjugated polyaromatic hydrocarbons and previously described helicenes.<sup>[2,3,13c]</sup> In  $\text{CH}_2\text{Cl}_2$  solution at r.t., **1a** displays classical structured blue fluorescence with a maximum ( $\lambda_{0-0}$ ) at 421 nm and a vibronic progression of  $1400 \text{ cm}^{-1}$  (quantum yield  $\Phi$  8.4% and fluorescence lifetime  $\tau$  6.6 ns, see Figure 2 and Figure S16; emission data for all compounds are summarized in Tables 1 and S3). A particularly interesting feature of fluorescent derivatives **P-(+)** and **M-(-)-1a** is that they exhibit CPL (Figures 2a)<sup>[3]</sup> with mirror-imaged spectra and respective luminescence dissymmetry ratios  $g_{\text{lum}}$  of  $+3.4 \times 10^{-3}$  and  $-3 \times 10^{-3}$  around the emission maximum (426 nm). These  $g_{\text{lum}}$  values are comparable to other fluorescent organic azahelicene derivatives.<sup>[3]</sup>

The UV-vis spectrum of **2a** shows a similar shape as **1a** and has a similar helicene-centered assignment. The CD spectrum of **P-2a** (Figure 1) displays two strong negative bands at 264 and 287 nm ( $\Delta\epsilon = -131, -130 \text{ M}^{-1} \text{ cm}^{-1}$ ) and several strong to moderate positive bands at 343, 386, 403, 429 nm ( $\Delta\epsilon = 212, 73, 41, 23 \text{ M}^{-1} \text{ cm}^{-1}$ ) that are  $\sim 10 \text{ nm}$  red-shifted compared to **P-1a** with the lower-energy  $\pi$ - $\pi^*$  excitations exhibiting significant intraligand charge transfer (ILCT) character. The MOs involved in the lower-energy excitations do not indicate a strong involvement of Pt 5d orbitals. The metal's dominant role is to render the structure of the chromophore rigid and to promote intersystem crossing (*vide infra*). A high molar rotation value is observed for **2a** (**P-2a**:  $[\phi]_D = +18730^\circ$  ( $\pm 5\%$ ), in  $\text{CH}_2\text{Cl}_2$ ,  $7 \times 10^{-5} \text{ M}$ , calc. B3LYP +19345). In contrast to **1a**, the rollover cycloplatinated helicene **2a** displays red phosphorescence at r.t. ( $\lambda_{\text{max}} = 547 \text{ nm}$ ,  $\Phi = 0.3\%$ ,  $\tau = 8.2 \mu\text{s}$ ), with no fluorescence band (Figures 2 and S18, Tables 1 and S3). Such behaviour is expected for cycloplatinated complexes due to strong spin-orbit coupling. The low quantum yield and estimated radiative rate constant of around  $200 \text{ s}^{-1}$  suggest that the phosphorescence is relatively inefficient, reflecting the decreasing contribution of the metal to the excited state, in agreement with the calculations. Phosphorescent derivatives **P-(+)** and **M-(-)-2a** are CPL active (Figure 2b),<sup>[3]</sup> and display mirror-imaged CPL spectra with  $g_{\text{lum}}$  values of  $+1 \times 10^{-3}$  and  $-1.1 \times 10^{-3}$  around the emission maximum (547 nm). These values are lower than those of previously published platina[6]helicenes ( $g_{\text{lum}} \sim 10^{-2}$ ),<sup>[3e]</sup> because the Pt center is less involved in the helical  $\pi$ -core of the molecule, as indicated by the calculations.<sup>[5c-f]</sup>

Upon protonation by an excess of "HBF<sub>4</sub>" in acetone, **P-[2a,H<sup>+</sup>][BF<sub>4</sub>]** and **M-[2a,H<sup>+</sup>][BF<sub>4</sub>]** were obtained quantitatively within two hours (Scheme 1). Their <sup>1</sup>H NMR spectra displayed

overall downfield shifted signals and the appearance of the NH<sup>+</sup> signal at 13.5 ppm (SI). Interestingly, the UV-vis spectra of protonated complexes **P-[2a,H<sup>+</sup>][BF<sub>4</sub>]** and **M-[2a,H<sup>+</sup>][BF<sub>4</sub>]** were significantly different from the non-protonated **P**- and **M-2a**, with a stronger broad band at longer wavelengths (380–510 nm,  $\lambda_{\text{max}} = 467 \text{ nm}$ ,  $\epsilon = 8260 \text{ M}^{-1} \text{ cm}^{-1}$ , Figure S9) than the corresponding neutral species (380–460 nm,  $\lambda_{\text{max}} = 429 \text{ nm}$ ,  $\epsilon = 5800 \text{ M}^{-1} \text{ cm}^{-1}$ ). Similarly, ECD spectra were substantially modified, with  $\sim 10 \text{ nm}$  red-shifted negative bands at 273 and 293 nm ( $\Delta\epsilon = -116, -86 \text{ M}^{-1} \text{ cm}^{-1}$ ), a less intense positive band at 345 nm ( $\Delta\epsilon = +135 \text{ M}^{-1} \text{ cm}^{-1}$ ), and strong band at 465 nm ( $\Delta\epsilon = +34 \text{ M}^{-1} \text{ cm}^{-1}$ ) for the **P-[2a,H<sup>+</sup>][BF<sub>4</sub>]** enantiomer (Figure 1). Note that several isosbestic points are appearing in the UV-vis and CD spectra upon successive addition of 0.1 eq of "HBF<sub>4</sub>" (see Figures S9 and S11). The protonation of enantiopure **M**- and **P**-proligands **1a** was also performed under the same conditions, i.e. by reacting with a slight excess of "HBF<sub>4</sub>" in either acetone or  $\text{CH}_2\text{Cl}_2$  thus yielding **M**- and **P-[1a,2H<sup>+</sup>][2BF<sub>4</sub>]** quantitatively. The <sup>1</sup>H NMR spectrum displays downfield shifts of all the signals, i.e. aza[6]helicene and pyridyl moiety (for example  $\Delta\delta = 0.6$  and  $0.2 \text{ ppm}$  for H<sup>6</sup> and H<sup>15</sup> respectively), consistent with the presence of two NH<sup>+</sup>.



**Figure 2.** a) CPL (top) and total emission (bottom) of fluorescent 3-(2-pyridyl)-4-aza[6]helicene **P-1a** (black), and **M-1a** (red) enantiomers to respectively **P-[1a,2H<sup>+</sup>][2BF<sub>4</sub>]** (green) and **M-[1a,2H<sup>+</sup>][2BF<sub>4</sub>]** (blue), at 426 nm and at 590 nm respectively, in  $\text{CH}_2\text{Cl}_2$  at r.t.; b) CPL (top) and total emission (bottom) of phosphorescent complex **P-2a** (black), and **M-2a** (red) enantiomers to respectively **P-[2a,H<sup>+</sup>][BF<sub>4</sub>]** (green) and **M-[2a,H<sup>+</sup>][BF<sub>4</sub>]** (blue), at 547 nm and at 555 nm respectively, in acetone at r.t. c) visual acid-base fluorescence switching of **1a**.

Compared to **1a**, the UV-vis spectrum of protonated **[1a,2H<sup>+</sup>][2BF<sub>4</sub>]** displays a new low-energy band of moderate intensity ( $\epsilon = 3500 \text{ M}^{-1} \text{ cm}^{-1}$ , Figure S8) between 430 and 530 nm and is slightly different in the 250–350 nm region. The ECD-active bands in the 250–350 nm region are significantly lowered (for example  $\Delta\epsilon = +44$  vs.  $111 \text{ M}^{-1} \text{ cm}^{-1}$  at 348 nm for **P-[1a,2H<sup>+</sup>][2BF<sub>4</sub>]** and **P-1a**, respectively) while a new ECD-active band has appeared around 430–530 nm ( $\Delta\epsilon = +14 \text{ M}^{-1} \text{ cm}^{-1}$  at 430 nm), Figure 1.<sup>[12a]</sup> The UV-vis and CD spectra are accompanied with the appearance of several isosbestic points upon successive addition of 0.1 eq of "HBF<sub>4</sub>" (see Figures S8 and S10). However, it was not possible to identify a mono-protonated intermediate, which suggests that both pyridyl cycles undergo protonation simultaneously. Intramolecular proton transfer between the two pyridyls may also occur.<sup>[12d]</sup> Note that



the charged protonated systems are very challenging for the calculations due to solvent-<sup>[12a]</sup> and counter-ion – effects (see SI). However, the most important trends upon protonation observed experimentally are correctly reproduced by the calculations, in particular the appearance of low-energy absorption and ECD bands. Protonation has a strong effect on the delocalization of the extended  $\pi$ -systems of both **1a** and **2a**. For instance, the new lowest-energy ECD band in **[2a,H<sup>+</sup>]** is assigned as dominantly H-L  $\pi$ - $\pi^*$  similar to **2a**, but unlike **2a** the transition is now a much more clear-cut CT case from the helicene moiety to the other side of the ligand. The frontier MOs of **2a** are conjugated through the pyridyl, but upon protonation the orbitals become spatially separated as demonstrated in Figure 1. Nucleus-independent chemical shift calculations for a model system as described in the SI suggest that the pyridyl becomes less aromatic upon protonation. Therefore, we attribute the increase in CT character to a loss of conjugation of the frontier orbitals caused by a reduction of aromatic character in the pyridyl moiety. The overall contribution of the H-L pair to the transition increases upon protonation, which further amplifies the increase of CT character (Table 2). Similar changes upon protonation can be observed for **1a**. The  $S_0$ - $S_1$  absorption becomes even more purely of H-L character here. Inspection of the orbital energies (Table S7) shows that protonation has a strongly stabilizing effect on the LUMO of **2a** and even more so on **1a**, and to a much lesser extent on the HOMO, reducing the H-L gap. The frontier MOs calculated for both **1a** and **2a** appear very similar (Figure 3). All exhibit large values of the LUMOs around the pendant pyridyl nitrogen while the HOMOs have nodes at this position. The same was found for MOs at the  $S_1$  and  $T_1$  optimized geometries (Figure S33, *vide infra*). Therefore, the appearance of the low-energy ECD bands upon protonation of both systems can be rationalized mainly by its impact on the LUMO and simultaneously the  $S_0$ - $S_1$  transition becoming more dominant in H-L character. The protonation has also an effect on the optical rotation. Molar rotations appeared lower for bis-protonated  $P$ -**[1a,2H<sup>+</sup>][2BF<sub>4</sub>]** ( $[\phi]_D = +10000$  ( $\pm 5\%$ ), in CH<sub>2</sub>Cl<sub>2</sub>,  $1.7 \times 10^{-4}$  M) than for  $P$ -**1a**, and decreased even more for the protonated complex  $P$ -**[2a,H<sup>+</sup>][BF<sub>4</sub>]** ( $[\phi]_D = +9145$  ( $\pm 5\%$ ), CH<sub>2</sub>Cl<sub>2</sub>,  $1.5 \times 10^{-5}$  M). Calculations (Table S4) indicate that the counterion(s) may play a role in these strong reductions. Furthermore, as depicted in Figure 4, successive addition of "HBF<sub>4</sub>" and NEt<sub>3</sub> in either acetone or CH<sub>2</sub>Cl<sub>2</sub> to 3-(2-pyridyl)-4-aza[6]helicene (**1a**) and its cycloplatinated complex **2a** enabled reversible and repeatable modification of the OR and ECD values, and hence the system constitutes a pH-triggered chiroptical switch.

The luminescence  $\lambda_{\text{max}}$  of **2a** undergoes much less of a change upon protonation than its ECD or the ECD and CPL of **1a** (Figure 2b). The calculated  $T_1$ - $S_0$  emission energies are likewise very similar for **2a** and its protonated form (Table 1) and in good agreement with experiment. Only for this transition we

found a decrease of H-L character upon protonation which renders the reduction of the H-L orbital energy gap due to protonation less important (Table 1), leading to a decrease of the calculated emission energy by only 0.1 eV. The estimated radiative rate constant remains around  $200 \text{ s}^{-1}$ , but the phosphorescence quantum yield is larger and the lifetime longer ( $\lambda_{\text{max}} = 555, 590 \text{ nm}$ ,  $\Phi = 2.7\%$ ,  $\tau = 120 \mu\text{s}$ ), suggesting that non-radiative decay pathways are impeded in the protonated form. The CPL activity is doubled in the protonated species ( $g_{\text{lum}} = +1.8 \times 10^{-3}$  and  $-2.2 \times 10^{-3}$  for  $P$ - and  $M$ -**[2a,H<sup>+</sup>][BF<sub>4</sub>]** respectively, Figure 2b).

Helicene **1a** shows a more striking change in its luminescence upon protonation. The emission is strongly bathochromically shifted, from  $\lambda_{\text{max}} = 426 \text{ nm}$  in **1a** to  $590 \text{ nm}$  in **[1a,2H<sup>+</sup>][2BF<sub>4</sub>]** (a shift of  $-0.8 \text{ eV}$ , in CH<sub>2</sub>Cl<sub>2</sub> solution at r.t., Figure 2a, Table S3). The calculations also produce a large bathochromic shift ( $-1.1 \text{ eV}$ ) for the  $S_1$ - $S_0$  emission upon protonation of **1a**, Table S8, mirroring a similar shift in the calculated  $S_0$ - $S_1$  excitation energies. The  $S_1$ - $S_0$  transitions afford slightly increasing contributions from the H-L pair upon protonation, meaning that the strong stabilization of the LUMO is more clearly reflected in the emission energy of **[1a,2H<sup>+</sup>]** than it is in the  $T_1$ - $S_0$  emission of **[2a,H<sup>+</sup>]**. The emission remains quite intense with a similar quantum yield and lifetime ( $\Phi = 8.2\%$ ,  $\tau = 5.4 \text{ ns}$ , Table S3). Similar  $g_{\text{lum}}$  values as for  $P$ - and  $M$ -**1a** were obtained for protonated samples ( $P$ -**[1a,2H<sup>+</sup>][BF<sub>4</sub>]**:  $+3.2 \times 10^{-3}$  and  $M$ -**[1a,2H<sup>+</sup>][BF<sub>4</sub>]**:  $-2.5 \times 10^{-3}$  at  $590 \text{ nm}$ ). Overall, this significant  $\lambda_{\text{em}}$  change from the blue to yellow fluorescence (Figure 2c) accompanied by CPL enables us to consider this system as a reversible CPL-active pH-triggered on-off chiroptical switch at either  $426$  or  $590 \text{ nm}$  by successive addition of either "HBF<sub>4</sub>" or Na<sub>2</sub>CO<sub>3</sub> / NEt<sub>3</sub> to acetone or CH<sub>2</sub>Cl<sub>2</sub> solution of 3-(2-pyridyl)-4-aza[6]helicene **1a**. To the best of our knowledge, this is the first example of a helicene-based multi-responsive acid-base chiroptical switch.<sup>[14]</sup>

## Conclusions

In conclusion, we have performed unprecedented pH-triggered switching of OR, CD and CPL activity using organic and organometallic helicene derivatives. The very large bathochromic shift of the emission observed upon protonation of azahelicene-bipy was theoretically rationalized by the decrease of aromaticity and stabilization of the LUMO level. Overall, this example illustrates the use of a chiral bipyridine ligand exhibiting "multiple personalities"<sup>[16]</sup> since it reveals original chiroptical and photophysical properties as well as  $N,C$  chelate behavior and it opens up new routes to chiral materials.

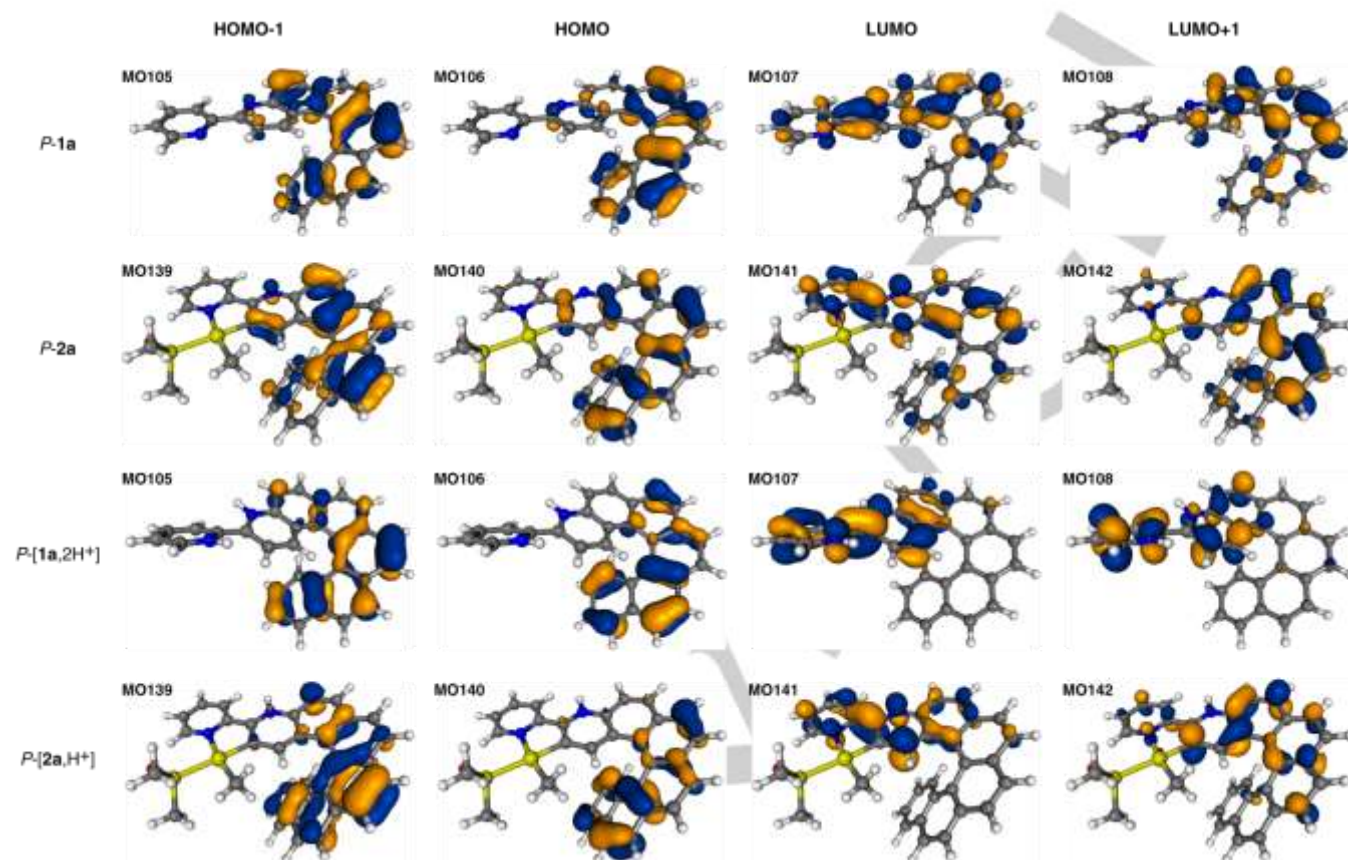


Figure 3. Isosurfaces (0.04 au) of selected MOs of **1a**, [**1a**,2H<sup>+</sup>] and **2a**, [**2a**,H<sup>+</sup>].

**Table 1.** Experimental and calculated emission data of ligand species **1a** and [**1a**,2H<sup>+</sup>] and of cycloplatinated complexes **2a** and [**2a**,H<sup>+</sup>]. Energies, in eV. Oscillator strength / rotary strength values in 10<sup>-40</sup> cgs are listed in parentheses.

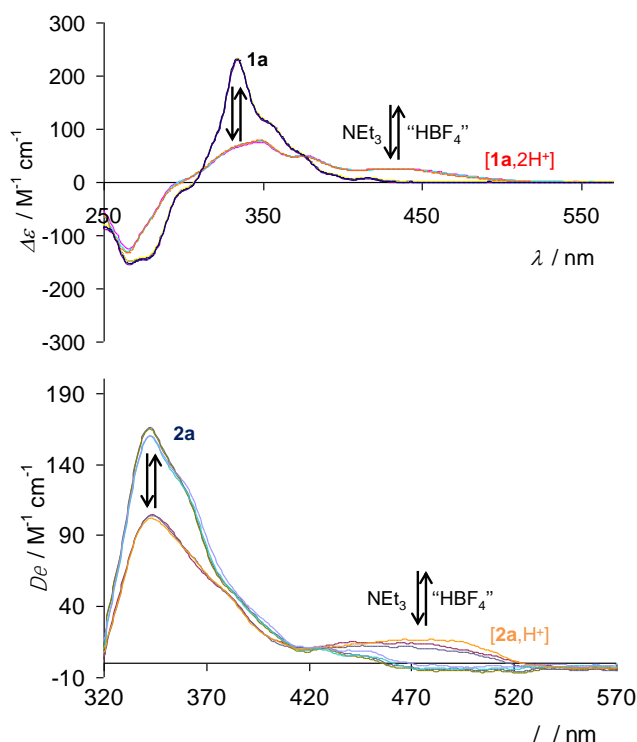
	<i>P</i> - <b>1a</b>	<i>P</i> -[ <b>1a</b> ,2H <sup>+</sup> ]-# <sup>a</sup>		<i>P</i> - <b>2a</b>	<i>P</i> -[ <b>2a</b> ,H <sup>+</sup> ]
		1	2		
Expt. <sup>b</sup>					
298 K	2.94, 2.79, 2.62	2.10		2.27, 2.12	2.23, 2.10
77 K	F: 2.97, 2.81, 2.63 P: 2.33, 2.15, 1.99	F: 3.13, 2.98, 2.81, 2.63 <sup>g</sup> P: 2.34, 2.15, 2.00 <sup>g</sup>		2.31, 2.13, 1.95	2.29, 2.10, 1.94 <sup>g</sup>
Calc. BHLYP/SV(P) <sup>c</sup>					
S <sub>1</sub> (TDDFT) <sup>d</sup>	2.99 (0.4642/427.88)	1.86 (0.1631/174.24)	1.87 (0.1741/194.33)	2.94 (0.5507/459.99)	2.66 (0.3444/268.69)
T <sub>1</sub> (TDDFT) <sup>e</sup>	2.18	1.49	1.50	2.16	2.08
T <sub>1</sub> (DFT) <sup>f</sup>	2.08	1.60	1.61	2.06	2.08

<sup>a</sup> Conformer #1: dihedral angle N-C-C'-N' of -150.0°, -170.5°, -175.7°, and -170.9° for S<sub>0</sub> ground state, S<sub>1</sub> excited state, T<sub>1</sub> excited state, and triplet configuration, respectively. Conformer #2: dihedral angle N-C-C'-N' of 151.0°, 171.5°, 172.2°, and 168.7° for S<sub>0</sub> ground state, S<sub>1</sub> excited state, T<sub>1</sub> excited state, and triplet configuration, respectively. <sup>b</sup> 298 K: DCM / acetone data for ligand / cycloplatinated species, 77 K: recorded in diethyl ether / isopentane / ethanol. F = fluorescence. P = phosphorescence. <sup>c</sup> DCM / acetone calculations for ligand / cycloplatinated species. <sup>d</sup> TDDFT S<sub>1</sub>-S<sub>0</sub> energy difference at TDDFT BHLYP/SV(P) optimized S<sub>1</sub> geometry. In parentheses oscillator strength / rotary strength values in 10<sup>-40</sup> cgs are listed. To convert to integrated CPL intensity, in cgs units of power output per molecule, the following expression can be used:  $\Delta I = 1.60041320 \cdot 10^{37} \cdot R_{\text{cgs}} \cdot E_{\text{cgs}}^4$ . <sup>e</sup> TDDFT T<sub>1</sub>-S<sub>0</sub> energy difference at TDDFT BHLYP/SV(P) optimized T<sub>1</sub> geometry. <sup>f</sup> TDDFT T<sub>1</sub>-S<sub>0</sub> energy difference at DFT BP/SV(P) optimized triplet configuration. <sup>g</sup> At 77K, the equilibrium B+H<sup>+</sup> ⇌ BH<sup>+</sup> is frozen.

**Table 2.** HOMO-to-LUMO character (in %) of  $S_0$ - $S_1$  absorption along with  $S_1$ - $S_0$  and  $T_1$ - $S_0$  emission transitions for ligand species **1a** and **[1a,2H<sup>+</sup>]** and of cycloplatinated complexes **2a** and **[2a,H<sup>+</sup>]**. B3LYP/SV(P) calculations with continuum solvent model for DCM.

	$S_0$ - $S_1$	$S_1$ - $S_0$	$T_1$ - $S_0$
<b>P-1a</b>	33.0	93.7	72.3
<b>P-[1a,2H<sup>+</sup>]<sup>a</sup></b>	91.7	96.5	76.0
		96.4	75.9
<b>P-2a</b>	53.8	92.3	68.9
<b>P-[2a,H<sup>+</sup>]</b>	75.5	90.1	61.6

<sup>a</sup> Results for two conformers are listed in the case of  $S_1$  and  $T_1$  excited states of **P-[1a,2H<sup>+</sup>]**, compare Table 1 (conformer #1 and #2).



**Figure 4.** Reversibility of the acid/base switching process by ECD spectroscopy for ligand **1a** (top) and complex **2a** (bottom) after several successive stoichiometric additions of acid and base.

## Experimental Section

Most experiments were performed using standard Schlenk techniques. Solvents were freshly distilled under argon from sodium/ benzophenone (THF) or from phosphorus pentoxide ( $\text{CH}_2\text{Cl}_2$ ). Starting materials were purchased from Aldrich. Column chromatography purifications were performed in air over silica gel (Merck Geduran 60, 0.063–0.200 mm). Irradiation reactions were conducted using a Heraeus TQ 700 mercury vapor lamp. NMR spectra  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  were recorded at room temperature on a Bruker AV400 spectrometer equipped with a QNP switchable probe  $^{13}\text{C}$ - $^{31}\text{P}$ - $^{19}\text{F}$ - $^1\text{H}$  and operating at proton resonance frequency of 400 MHz. Chemical shifts are reported in parts per million (ppm) relative to  $\text{Me}_4\text{Si}$  as external standard. Assignment of proton atoms is based on COSY experiment.  $^{31}\text{P}$  NMR downfield chemical shifts are

expressed with a positive sign, in ppm, relative to external 85%  $\text{H}_3\text{PO}_4$ . All spectra were obtained using deuterated dichloromethane or chloroform as solvents. The terms s, d, t, q, m indicate respectively singlet, doublet, triplet, quartet, multiplet; b is for broad and, dd is doublet of doublets, dt doublet of triplets, td triplet of doublets. Assignment of proton atoms is based on COSY, HMBC, HMQC experiments. Carbon atoms were assigned based on DEPT-135 experiments. Elemental analyses were performed by the CRMPO, University of Rennes 1. Specific rotations (in  $\text{deg cm}^2\text{g}^{-1}$ ) were measured in a 1 dm thermostated quartz cell on a Perkin Elmer-341 polarimeter. Circular dichroism (in  $\text{M}^{-1}\text{cm}^{-1}$ ) was measured on a Jasco J-815 Circular Dichroism Spectrometer (IFR140 facility - Biosit platform - Université de Rennes 1). UV/vis spectroscopy was conducted on a Varian Cary 5000 spectrometer. 2,2'-Bipyridine-6-carbaldehyde,<sup>[17,18]</sup> (benzo[c]phenanthren-3-ylmethyl)-triphenylphosphonium bromide<sup>[7]</sup> and *cis*-(*dms*)<sub>2</sub>PtMe<sub>2</sub><sup>[19]</sup> were prepared according to literature procedures.

### Racemic 3-(2-pyridyl)-4-aza[6]helicene (**±**)-**1a**.

1) A solution of (benzo[c]phenanthren-3-ylmethyl)triphenylphosphonium bromide<sup>[7]</sup> (1.465 g, 2.5 mmol) in 40 ml of anhydrous THF was placed in a Schlenk tube under argon and cooled to  $-78^\circ\text{C}$  for 5 minutes. To the stirred suspension *n*-BuLi (2.5 solution in hexanes, 1 ml, 26 mmol) was added dropwise. The reaction mixture turned deep red then warmed to room temperature slowly. After 45 minutes, the reaction mixture was cooled again to  $-78^\circ\text{C}$ , then 2,2'-bipyridine-6-carbaldehyde<sup>[17,18]</sup> (440 mg, 2.39 mmol) was added in one portion; the reaction mixture was warmed to room temperature and the color turned yellow white with stirring for 3 hours. The reaction mixture was filtered over celite and concentrated under vacuum, and the crude oily product was purified by column chromatography (silica gel, heptane / ethyl acetate 7:3) to give the olefine (*cis* and *trans* mixture) as a yellow solid (890 mg, 92%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.26 (1H, s), 9.20 (1H, d,  $J = 8.5$  Hz), 9.17 (0.45H, s), 8.75 (1H, d,  $J = 3.6$  Hz), 8.72 (0.5H, s), 8.65 (1.4H, d,  $J = 7.8$  Hz), 8.33 (1.4H, t,  $J = 7.4$  Hz), 8.15-7.73 (14.5H, m), 7.68 (2H, t,  $J = 7.8$  Hz), 7.53 (1H, dd,  $J = 14.4$ , 7.3 Hz), 7.48-7.31 (4H, m), 7.28 (0.3H, s), 7.26-7.19 (0.4H, m), 7.16 (0.4H, d,  $J = 12.3$  Hz), 6.93 (0.4H, d,  $J = 12.2$  Hz). Elemental analysis, calcd. (%) for  $\text{C}_{30}\text{H}_{20}\text{N}_2$ : C, 88.21; H, 4.93; N, 6.86; found C 87.98, H 4.85, N 6.80.

2) The mixture of *cis* and *trans* olefin 6-(2-(benzo[c]phenanthren-2-yl)vinyl)-2,2'-bipyridine (100 mg) in 1 L toluene/THF (9:1) was irradiated for 5 hrs in the presence of catalytic amount of iodine using a 700W mercury vapor lamp. Then the solvent was stripped off and the crude product was purified over silica gel (heptane / ethyl acetate 8:2) to give (**±**)-**1a** as a yellow solid (90 mg, 90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  8.56 (1H, m,  $\text{H}^3$ ), 8.49 - 8.53 (1H, m,  $\text{H}^6$ ), 8.14 (2H, s), 7.94 - 8.03 (4H, m), 7.90 (2H, s), 7.86 (1H, d,  $J = 8.9$  Hz), 7.80 (1H, d,  $J = 8$  Hz,  $\text{H}^{13}$ ), 7.79-7.74 (m, 1H,  $\text{H}^4$ ), 7.65 (1H, d,  $J = 8.7$  Hz), 7.57 (d,  $J = 9$  Hz, 1H,  $\text{H}^{16}$ ), 7.22 (1H, ddd,  $J = 7.3$ , 4.8, 1.1 Hz,  $\text{H}^5$ ), 7.15 (1H, ddd,  $J = 8$ , 6.9, 1.1 Hz,  $\text{H}^{14}$ ), 6.64 (1H, ddd,  $J = 8.5$ , 6.9, 1.4 Hz, 1H,  $\text{H}^{15}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  156.33 (C), 154.86 (C), 149.45 (CH), 147.54 (C), 137.13 (CH), 135.94 (CH), 133.69 (C), 132.59 (C), 132.07 (C), 131.74 (C), 130.63 (CH), 129.88 (C), 129.81 (CH), 128.61 (CH), 128.31 (CH), 128.12 (CH), 128.04 (CH), 128.03 (CH), 127.97 (C), 127.60 (CH), 127.42 (CH), 126.54 (CH), 126.15 (CH), 125.77 (C), 125.58 (CH), 124.39 (C), 124.27 (CH), 121.54 (CH), 116.94 (CH). Elemental analysis, calcd. (%) for  $\text{C}_{30}\text{H}_{18}\text{N}_2$ : C, 88.64; H, 4.46; N, 6.89; found C 88.55, H 4.39, N 6.83.

**3-Pyridinium-4-azonia[6]helicene [1a,2H<sup>+</sup>][2BF<sub>4</sub>]**. Compound **1a** (10 mg, 0.024 mmol) was dissolved in 4 ml  $\text{CH}_2\text{Cl}_2$  then  $[\text{H}_2\text{O}.\text{HBF}_4]_2[18\text{C}6]^{[15]}$  (0.027 mmol, 13 mg) was added and the reaction mixture was stirred for 2 hours at room temperature.  $\text{CH}_2\text{Cl}_2$  was evaporated to small volume, and then ether was added to observe yellow precipitate that was filtrated and washed with ether to remove the excess acid. Finally, the precipitate was dried under vacuum to obtain **[1a,2H<sup>+</sup>][2BF<sub>4</sub>]** as yellow-orange powder (12.6 mg, 90%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.08 - 9.15 (1H, m,  $\text{H}^6$ ), 8.47 - 8.59 (2H, AB,  $J = 9.1$  Hz), 8.34 - 8.43 (2H, m), 8.27 (2H, d,  $J = 8.3$  Hz), 8.12 - 8.19 (3H, m), 8.02 - 8.09 (2H, m), 7.94 (1H, dd,  $J = 8.10$ , 0.8 Hz,  $\text{H}^{13}$ ), 7.88 (1H, ddd,  $J = 7.6$ , 5.4, 1.1 Hz,  $\text{H}^5$ ), 7.65 (1H, d,  $J = 8.6$  Hz,  $\text{H}^{16}$ ), 7.47 (1H, d,  $J =$



9.0 Hz), 7.29 (1 H, ddd,  $J = 8, 6.9, 1.1$  Hz,  $H^{14}$ ), 6.83 (1 H, ddd,  $J = 8.5, 7.0, 1.4$  Hz,  $H^{15}$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  147.07 (C), 146.53 (CH), 144.34 (CH), 144.25 (C), 140.42 (CH), 135.39 (CH), 134.28 (C) 132.78 (C), 132.68 (C), 132.62 (C), 130.30 (1 CH), 129.19 (CH), 129.18 (CH), 129.06 (C), 128.68 (CH), 127.99 (CH), 127.70 (CH), 127.68 (CH), 127.56 (CH), 127.40 (C), 127.26 (C), 126.80 (C), 126.66 (CH), 126.61 (CH), 126.30 (CH), 125.81 (CH), 124.10 (C), 123.55 (CH), 116.10 (CH). One C is missing. Elemental analysis, calcd. (%) for  $\text{C}_{30}\text{H}_{20}\text{B}_2\text{F}_8\text{N}_2$ : C, 61.90; H, 3.46; N, 4.81; found C 62.63, H 3.56, N 4.57.

### 3-Pyridyl-4-aza[4]helicene 1b.

1) A solution of 2-methylnaphthyltriphenylphosphonium bromide (433 mg, 0.89 mmol) in 15 ml of anhydrous THF was placed in a Schlenk tube under argon and cooled to  $-78^\circ\text{C}$ . To the stirred suspension  $n\text{-BuLi}$  (1.6N solution in hexanes, 0.58 ml, 0.93 mmol) was added dropwise. The reaction mixture turned deep red then warmed to room temperature slowly. After 45 minutes, the reaction mixture was cooled again to  $-78^\circ\text{C}$ . Then 2,2'-bipyridine-6-carbaldehyde<sup>[17,18]</sup> (157 mg, 0.85 mmol) was added in one portion; the reaction mixture was warmed to room temperature and the color turned yellow white with stirring overnight. The reaction mixture was filtered over celite and concentrated under vacuum, and the crude oily product was purified by column chromatography (silica gel, heptane / ethyl acetate 8:2) to give the olefin (*cis* and *trans* mixture) as a yellow solid (215 mg, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.63 (1 H, d,  $J = 4.0$  Hz), 8.51 - 8.58 (2 H, m), 8.22 (1 H, d,  $J = 8.0$  Hz), 8.14 (1 H, d,  $J = 8.0$  Hz), 7.85 - 7.95 (3 H, m), 7.70 - 7.84 (7 H, m), 7.59 - 7.69 (2 H, m), 7.53 (1 H, t,  $J = 7.9$  Hz), 7.34 - 7.48 (7 H, m), 7.23 - 7.34 (2 H, m), 7.11 - 7.17 (2 H, m), 6.96 (1 H, d,  $J = 12.3$  Hz), 6.76 (1 H, d,  $J = 12.3$  Hz). Elemental analysis, calcd. (%) for  $\text{C}_{22}\text{H}_{16}\text{N}_2$ : C, 85.69; H, 5.23; N, 9.08; found C 84.50, H 5.19, N 9.03.

2) The mixture of *cis* and *trans* olefin 6-(2-(benzo[*c*]phenanthren-2-yl)vinyl)-2,2'-bipyridine (500 mg) in 700 mL toluene/THF (9:1) was irradiated for 15 hrs in the presence of catalytic amount of iodine using a 150W mercury vapor lamp. Then the solvent was stripped off and the crude product was purified over silica gel (heptane / ethyl acetate; 9:1) to give **1b** as yellow solid (370 mg, 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.41 (1 H, d,  $J = 9$  Hz,  $H^1$ ), 8.98 (1 H, d,  $J = 8.1$  Hz,  $H^{12}$ ), 8.59 - 8.68 (3 H, m,  $H^6, H^2, H^2$ ), 8.00 - 8.12 (2H, AB,  $J = 8.7$  Hz,  $H^5, H^6$ ) 7.98 (1 H, dd,  $J = 7.9, 1.7$  Hz,  $H^{13}$ ), 7.78 - 7.89 (2 H, AB,  $J = 8.5$  Hz,  $H^{7,8}$ ), 7.81 (1 H, m,  $H^4$ ), 7.63 - 7.69 (1 H, m,  $H^{11}$ ), 7.56 - 7.62 (1 H, m,  $H^{10}$ ), 7.29 (1 H, ddd,  $J = 7.4, 4.8, 1.3$  Hz,  $H^5$ ).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  156.46 (C), 155.23 (C), 149.67 (CH), 148.95 (C), 137.28 (CH), 136.67 (CH), 133.98 (C), 131.53 (C), 131.11 (CH), 130.56 (C), 129.43 (CH), 129.20 (CH), 128.67 (CH), 127.86 (CH), 127.31 (C), 127.15 (CH), 127.08 (CH), 126.75 (CH), 125.87 (C), 124.45 (CH), 121.80 (CH), 118.36 (CH). Elemental analysis, calcd. (%) for  $\text{C}_{22}\text{H}_{14}\text{N}_2$ : C, 86.25; H, 4.61; N, 9.14; found C 86.12, H 4.55, N 9.05.

**Complex 2b.** To a solution of *cis*-( $\text{dmsO}$ )<sub>2</sub>PtMe<sub>2</sub><sup>[19]</sup> (20 mg, 0.05 mmol) in acetone (5 mL) was added 16 mg of proligand **1b** (0.05 mmol). The stirred solution was heated to  $50^\circ\text{C}$  and kept under a nitrogen atmosphere. After 5 h the mixture was cooled to room temperature, concentrated to small volume, and treated with pentane to form a precipitate. The solid was filtered off, washed with pentane, and vacuum-pumped to give the analytical sample **2b** (27 mg, 90%) as an orange solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.77 (1 H, d,  $J_{\text{Pt-H}} = 6.0$  Hz,  $^3J_{\text{Pt-H}} = 12.1$  Hz,  $H^6$ ), 9.54 (1 H, s,  $^3J_{\text{Pt-H}} = 32$  Hz,  $H^1$ ), 9.04 (1 H, d,  $J = 8.5$  Hz,  $H^{12}$ ), 8.53 (1 H, d,  $J = 7.3$  Hz,  $H^3$ ), 7.95 - 8.04 (3 H, m,  $H^{5,4,9}$ ), 7.90 - 7.94 (1 H, m,  $H^6$ ), 7.78-7.88 (2 H, AB,  $J = 8.5$  Hz,  $H^{7,8}$ ), 7.65 (1 H, t,  $J = 6.9$  Hz,  $H^{11}$ ), 7.48 (1 H, t,  $J = 7.3$  Hz,  $H^{10}$ ), 7.39 (1 H, t,  $J = 5.8$  Hz,  $H^5$ ), 3.15 - 3.25 (6 H, s,  $^3J_{\text{Pt-H}} = 18.4$  Hz,  $H_{\text{dmsO}}$ ), 0.78 (3 H, s,  $^2J_{\text{Pt-H}} = 83$  Hz,  $H_{\text{Me-Pt}}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  164.75 (C), 161.97 (C), 150.64 (CH), 146.61 (C), 141.42 (C), 138.93 (CH), 138.56 (CH), 133.51 (C), 131.15 (C), 130.48 (C), 128.98 (CH), 128.75 (CH), 128.60 (CH), 128.08 (CH), 127.78 (CH), 127.02 (C), 126.72 (CH), 126.24 (CH), 126.09 (C), 125.98 (CH), 125.11 (CH), 122.13 (CH), 43.82 (2CH<sub>3</sub>), -13.52 (CH<sub>3</sub>). Elemental analysis, calcd. (%) for  $\text{C}_{25}\text{H}_{22}\text{N}_2\text{OPtS}$ : C 50.58; H, 3.74; found C, 50.47, H 3.68.

**Complex Pt(1b)Cl(dmsO).** To a solution of **2b** (40 mg, 0.067 mmol) in 8 mL of acetone was added with vigorous stirring 0.34 mL of dmsO and 0.67 mL of aqueous 0.1 M HCl (0.067 mmol). After 8 h the solution was concentrated to a small volume then extracted with  $\text{CH}_2\text{Cl}_2$ , dried with  $\text{Na}_2\text{SO}_4$ , and concentrated to a small volume. The residue was then treated with pentane to form a precipitate which was filtered, washed with pentane, and vacuum-pumped to give the analytical sample Pt(1b)Cl(dmsO) (29 mg, 70%) as a yellow solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  10.17 (1 H, s,  $^3J_{\text{Pt-H}} = 25$  Hz,  $H^1$ ), 9.64 (1 H, d,  $J = 6.0$  Hz,  $H^6$ ), 9.13 (1 H, d,  $J = 8.3$  Hz,  $H^{12}$ ), 8.46 (1 H, d,  $J = 9.0$  Hz,  $H^3$ ), 7.91 - 8.07 (4 H, m,  $H^{5,6,4,9}$ ), 7.77 - 7.89 (2H, AB,  $J = 8.5$  Hz,  $H^{7,8}$ ), 7.53 - 7.67 (2 H, m,  $H^{10,11}$ ), 7.43 (1 H, t,  $J = 6.0$  Hz,  $H^5$ ), 3.62 (6 H, s,  $^3J_{\text{Pt-H}} = 12$  Hz,  $H_{\text{dmsO}}$ ). Elemental analysis, calcd. (%) for  $\text{C}_{24}\text{H}_{19}\text{ClN}_2\text{OPtS}$ : C, 46.95; H, 3.12; found C 46.78, H 3.01.

**Complex 3b.** To a solution of Pt(1b)Cl(dmsO) (14.6 mg, 0.024 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added 6.2 mg of  $\text{PPh}_3$  (0.024 mmol). The stirred solution was kept under a nitrogen atmosphere. After 2 h the mixture was concentrated to small volume and treated with pentane to form a precipitate. The solid was filtered off, washed with pentane, and vacuum-pumped to give the analytical sample **3b** as a yellow solid (19 mg, 98%) that was crystallized with slow diffusion of pentane into  $\text{CH}_2\text{Cl}_2$  solution.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.86 (1 H, m,  $H^6$ ), 8.52 (1 H, d,  $J = 8.3$  Hz,  $H^3$ ), 8.35 (1 H, s,  $^3J_{\text{Pt-H}} = 56$  Hz,  $H^1$ ), 8.01 - 8.08 (1 H, m,  $H^4$ ), 7.89 (1 H, d,  $J = 9$  Hz), 7.74 - 7.81 (6 H, m), 7.71 (1 H, d,  $J = 8.3$  Hz,  $H^{12}$ ), 7.66 (1 H, d,  $J = 8.8$  Hz), 7.53 - 7.60 (2 H, m), 7.45 - 7.52 (1 H, m), 7.36 - 7.43 (1 H, m), 7.31 (1 H, ddd,  $J = 8.1, 6.9, 1$  Hz,  $H^5$ ), 7.23 - 7.29 (3 H, m), 7.11 - 7.20 (6 H, m), 6.40 (1 H, ddd,  $J = 8.4, 7.0, 1.4$  Hz,  $H^{11}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  163.27 (CH), 148.5 (C), 145.05 (C), 142.30 (CH), 140.12 (CH), 135.32 - 135.87 (6CH), 133.0 (C), 130.97 (CH), 130.96 (CH), 129.91 (C), 129.53 (C), 129.29 (C), 128.94 (CH), 128.79 (CH), 128.60 (C), 128.53 (C), 128.41 (C), 127.7 - 128.14 (9CH), 127.36 (CH), 126.56 (C), 126.35 (CH), 126.09 (C), 126.03 (CH), 125.44 (CH), 125.21 (C), 124.74 (CH), 122.14 (CH).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  22.70 ( $J_{\text{Pt-P}} = 4301.5$  Hz). Elemental analysis, calcd. (%) for  $\text{C}_{40}\text{H}_{28}\text{ClN}_2\text{PPt}$ : C, 60.19; H, 3.54; found C 60.03, H 3.45.

**Complexes P- and M-2a.** To a solution of *cis*-( $\text{dmsO}$ )<sub>2</sub>PtMe<sub>2</sub><sup>[19]</sup> (20 mg, 0.05 mmol) in acetone (5 mL) was added 21.3 mg of **P-1a** (0.05 mmol). The stirred solution was heated to  $50^\circ\text{C}$  and kept under a nitrogen atmosphere. After 5 h the mixture was cooled to room temperature, concentrated to small volume, and treated with pentane to form a precipitate. The solid was filtered off, washed with pentane, and vacuum-pumped to give the analytical sample **P-2a** (31 mg, 90%) as an orange solid. The same procedure was used to prepare **M-2a** from **M-1a**.  $^1\text{H}$  NMR (400 MHz  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  9.48 - 9.57 (1 H, m,  $^3J_{\text{Pt-H}} = 20$  Hz,  $H^6$ ), 8.36 - 8.41 (1 H, m), 8.10 (1 H, s,  $^3J_{\text{Pt-H}} = 62.5$  Hz), 7.98 (2 H, s), 7.80 - 7.96 (7 H, m), 7.72 (1 H, dd,  $J = 8.1, 1.40$  Hz), 7.61 - 7.67 (1 H, m), 7.24 (1 H, ddd,  $J = 7.4, 5.6, 1.5$  Hz), 7.13 (1 H, ddd,  $J = 8, 6.9, 1.1$  Hz), 6.63 (1 H, ddd,  $J = 8.5, 6.9, 1.4$  Hz), 2.99 (3 H, s,  $^3J_{\text{Pt-H}} = 18$  Hz), 2.89 (3 H, s,  $^3J_{\text{Pt-H}} = 18$  Hz), -0.38 (3 H, s,  $^2J_{\text{Pt-H}} = 83.3$  Hz).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  162.18 (C), 148.49 (CH), 150.80 (CH), 145.68 (C), 140.90 (C), 138.69 (CH), 138.41 (CH), 133.56 (C), 131.73 (C), 131.70 (C), 130.04 (C), 129.63 (CH), 128.80 (CH), 128.44 (CH), 128.42 (C), 128.23 (C), 128.16 (CH), 128.01 (CH), 127.80 (CH), 127.56 (CH), 127.50 (CH), 127.21 (C), 127.17 (CH), 126.41 (CH), 126.05 (CH), 126.03 (C), 125.28 (2CH), 124.62 (C), 122.24 (CH), 44.05 (CH<sub>3</sub>), 43.88 (CH<sub>3</sub>), -14.21 (CH<sub>3</sub>). Elemental analysis, calcd. (%) for  $\text{C}_{33}\text{H}_{26}\text{N}_2\text{OPtS}$ : C, 57.13; H, 3.78; found C 57.05, H 3.72.

**Complexes P- and M-[2a,H<sup>+</sup>][BF<sub>4</sub>].** To a solution of **P-2a** (5 mg, 7.2  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added 3 mg of  $[\text{H}_2\text{O} \cdot \text{HBF}_4]_2[\text{18C6}]$ <sup>[15]</sup> (2 mg, 4  $\mu\text{mol}$ ). After 2 h the mixture was concentrated to small volume and treated with  $\text{Et}_2\text{O}$  to form a precipitate. The solid was filtered off, washed with  $\text{Et}_2\text{O}$ , and vacuum pumped to give the analytical sample **P-[2a,H<sup>+</sup>][BF<sub>4</sub>]** (5.2 mg, 92%) as a bright-orange solid. The same procedure was used to prepare **M-[2a,H<sup>+</sup>][BF<sub>4</sub>]** from **M-2a**.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  13.58 (1 H, br, *NH*), 9.87 (1 H, d,  $J = 5.5$  Hz,  $^3J_{\text{Pt-H}} = 20$



Hz,  $H^6$ ), 9.00 (1 H, s,  $^3J_{\text{Pt-H}} = 64.2$  Hz,  $H^1$ ), 8.79 (1 H, d,  $J = 7.8$  Hz,  $H^3$ ), 8.52 (2 H, s), 8.21 - 8.33 (2 H, m), 8.06 - 8.17 (2 H, m), 7.95 - 8.05 (2 H, m), 7.88 (1 H, d,  $J = 7.5$  Hz,  $H^{13}$ ), 7.59 - 7.70 (2 H, m,  $H^{5,16}$ ), 7.29 (1 H, m,  $H^{14}$ ), 6.87 (1 H, m,  $H^{15}$ ), 3.16 (3 H, s,  $^3J_{\text{Pt-H}} = 21$  Hz), 3.06 (3 H, s,  $^3J_{\text{Pt-H}} = 21$  Hz,  $H_{\text{dmsd}}$ ), -0.21 (3 H, s,  $^3J_{\text{Pt-H}} = 82$  Hz,  $H_{\text{Me-Pt}}$ ).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  152.03(CH), 146.98 (CH), 140.99 (C), 140.22 (CH), 136.03 (C), 135.53 (CH), 134.1 (C), 134.14 (C), 133.01 (C), 132.18 (C), 131.70 (C), 129.94 (CH), 129.11 (CH), 128.88 (CH), 128.31 (C), 128.15 (CH), 128.01 (CH), 127.92 (CH), 127.25 (CH), 127.20 (C), 127.11 (CH), 126.75 (C), 126.71 (CH), 126.23 (CH), 126.15 (C), 126.04 (CH), 125.88 (C), 123.59 (C), 123.43 (CH), 120.03 (CH), 43.76 ( $\text{CH}_3$ ), 43.73 ( $\text{CH}_3$ ), -13.81 ( $\text{CH}_3$ ). Elemental analysis, calcd. (%) for  $\text{C}_{33}\text{H}_{27}\text{BF}_4\text{N}_2\text{OPTS}$ : C, 50.72; H, 3.48; N, 3.58; found C 50.83, H 3.53, N 3.49.

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